Research and Development of Reactively Evaporated a-Si Photovoltaic Cells

RENEWABLE ENERGY BRANCH

PREPARED FOR:

Renewable Energy Branch
Energy, Mines and Resources Canada
Ottawa Canada
SSC Contract File No: 24ST.23216-6-6188
July 29, 1987.

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Acknowledgements

The investigators would like to thank Paul Andry for his assistance with the preparation of many of the samples and devices.

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Preface

Conventionally the best a-Si:H suitable for use in solar cells has been made by the glow discharge deposition of silicon or plasma-enhanced vapour deposition using silane gas (SiH_4). However, Good quality films have been made by other methods. All of these methods employ highly toxic and corrosive materials. These a-Si:H films possess a reversible electronic instability first reported by Staebler and Wronski (Staebler and Wronski, 1977) and often referred to as the S-W effect. Although much theoretical and experimental work has been done, the origin of the instability is not yet definitively established and the actual mechanism is still in doubt. The most convincing evidence seems to suggest that this instability is due to a native defect (the so-called D^0 center) which arises either due to a dangling bond (a T^3 complex) or a floating bond (a T^5 complex) (Pantelides, 1986) or both. These are respectively 3-fold and 5-fold coordinated silicon atoms in the a-Si:H. More and more authors believe this is the case.

The presence of this instability reduces the possible efficiencies that can be reasonably expected (Madan, 1986) for a-Si:H solar cells, from 18% to less than 10%. Although the extent of the degradation can be reduced by cell geometry, it is believed that cells with efficiencies >10% can only be achieved using tandem cells made with

a-Si:H and its alloys. A significant improvement could be achieved if stable a-Si can be produced. Success in this venture would lead to a multibillion dollar industry worldwide.

It is very desirable to eliminate or reduce this reversible instability problem if possible. If it arises from the native defects in a-Si one can reduce or eliminate it by reducing or eliminating these defects in the material, or by incorporating other materials. These added impurities can be expected to "pin" the defects (the so called D^0 center complexes). It is known that some alloys are more stable than a-Si:H and that the amount of the additive can alter the electronic properties. The object of this study was to produce a stable a-Si:H alloy with acceptable critical electronic characteristics that would permit the fabrication of good solar cells. The second guiding principle for this project is to do this by an inexpensive method that uses relatively safe materials and does not harm the environment.

This report is prepared for the Solar Energy Division of the Department of Energy, Mines and Resources and it reviews the technological progress made since September 1986. It is intended for scientists and engineers who may benefit from the scientific and technical advances made during this period. This project is complementary to the other projects in, and forms a part of the Solar Energy Development Program of EMR.

There are a number of significant achievements noted here.

It has been demonstrated definitely that a reactive evaporation process can be used to fabricate both p-type and n-type a-Si:H by co-evaporating boron and phosphorus. It has also been demonstrated for the first time that an all amorphous a-Si:H diode can be prepared by a reactive evaporation process using relatively safe materials.

Abstract

The long term objective of this work is to produce a stable, efficient a-Si solar cell by a relatively safe inexpensive method. A reactive evaporation process has been developed which permits the fabrication of a-Si:H, p-i-n diodes and possibly solar cells. The method makes use of a high vacuum system ($1x10^{-8}$ torr operating base pressure) with a residual gas analyzer, a precision leak valve and a variety of resistively heated, as well as electron beam sources. Films were prepared under carefully monitored and controlled conditions and characterized electrically, optically and in a limited number of cases structurally. Completed working devices have only recently been obtained and to date have been studied using only current voltage characteristics.

It has been demonstrated that vacuum deposited a-Si:H can be doped by co-evaporating boron or phosphorus and a p-i-n diode has been fabricated using this technique.

The work has raised a number of questions that require further research and these are identified.

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Executive Summary

The initial work on the project was done using reactive evaporation in ammonia to create "intrinsic-like" a-Si. This material had room temperature conductivities of 10^{-12} Scm^{-1}. The high temperature activation energy for these samples was about 0.9 eV and the optical bandgap was 1.8 to 2.0 eV. The co-evaporation of antimony or indium to yield n-type or p-type layers produced an appropriate increase in the conductivity. It was not until the Seebeck data was obtained that the indium doped samples were found to be n-type instead of p-type as expected! The work with the NH_3 compensated Si was discontinued and SiH_4 was introduced as the reactive compensating gas. The clarification of problems encountered with NH_3 compensation and indium and antimony doping of the a-Si material have added greatly to our understanding of the reactive evaporation process.

Reactive evaporation using SiH_4 instead of NH_3 proved to be more difficult. The SiH_4 has a lower sticking coefficient than NH_3 and higher ambient pressures of silane are required. Again antimony and indium were used to dope the "intrinsic" material but the indium doped samples were again <u>not</u> p-type. After several attempts, using different anneal procedures, substrate temperatures (T_s), etc. it was decided that indium was not acceptable. Experiments showed that the low sublimation

temperature of the antimony resulted in re-evaporation from the substrate when high substrate temperatures (T_s= 600 K) were used. The Arrhenius plots of the conductivity and temperature of the indium and antimony doped samples were not linear, which suggests that there is not a well defined energy level for either dopant. To solve these problems, phosphorus and boron were used as dopants. These had not been used previously because phosphorus is difficult to work with and boron has a very high evaporation temperature.

The first successful device prepared was a p-i-n structure using silane compensation and boron and phosphorus dopants. Subsequent work has continued on the production and characterization of a solar cell with this structure. Schottky barrier and p-n devices have not yet been attempted with silane compensated material. It is felt that because this material can be used to produced p-i-n devices, it will be possible to make other devices with silane compensated a-Si.

The first devices were made using Mo contacts with an n-type bottom layer, an intrinsic middle layer and a p-type top layer yielding an n-i-p structure. Various values of T_s (substrate temperature during deposition) were tried using several different anneal procedures. It was found that T_s= 420 K with a fairly long anneal time at 500 K produced working devices.

The difficulty in reproducing p-i-n devices led us to suspect that the a-Si:H was not fully hydrogen compensated. The final weeks of

this contract were used to produce fully compensated "intrinsic-like" material so that doped samples, yielding predictable properties, could be prepared. We believe that we have achieved this, but no solar cells have been fabricated with the fully compensated a-Si:H.

Resume

Final Report

SSC File No. 24ST.23216-6-6188
Serial No. 23216-6-6188/01-ST

1. Introduction

The goal of this project was to prepare a-Si solar cells using reactive evaporation techniques which employ relatively safe materials. The current technology used in the preparation of a-Si solar cells involves expensive facilities to accommodate the toxic materials required. To make the a-Si solar cells economically feasible on a large scale, it will be necessary to reduce the production cost. More importantly than the high cost, the devices prepared by current techniques have photoelectronic instabilities which are not yet fully understood. This instability (Staebler-Wronski instability) degrades the cell performance, often to unacceptable levels. It is well known that a-Si made by different methods can have different micro-structures and different electrical properties. It is reasonable to expect that a reactive evaporation process which can incorporate a variety of materials (e.g. H, N, O, P, etc.) into a growing film, might produce a more stable material. The current contract represents an attempt to achieve two things. The first was to demonstrate that an all amorphous device can be fabricated by the reactive evaporation process. The second purpose was to investigate the stability of the a-Si:H material and if it is not stable, incorporate selective impurities that might stabilize it.

The first step has been achieved and work is continuing on the investigation of the stability.

2. Objectives

The initial objective of this work was to develop the vacuum deposition techniques required to produce intrinsic, p-type and n-type a-Si:H thin films. These thin films were also electrically and optically characterized. The next objective was to produce all amorphous silicon devices from these materials. Finally, solar cells were to be produced and these would then be characterized and optimized.

3. Method

3.1 The Deposition System

The deposition system consists of an 18" diameter working chamber, with a top and bottom plate providing many electrical, gas, mechanical and water feedthroughs. Figure 1 shows a schematic representation of the chamber and its main components. The system is evacuated using a 6" high speed Varian diffusion pump which is backed by a direct drive high capacity mechanical pump. The diffusion pump is assisted by a long life liquid nitrogen cold trap. The vacuum chamber is pumped over night with bakeout lamps turned on. The substrate is cleaned using Alcanox soap in distilled water, followed by ultrasonic rinses in distilled water and spectroscopic grade ethanol. The substrate is then held at 470 K while the chamber pumps down to outgas any residual contaminants. The working base pressure of the system is about $1x10^{-8}$ torr with the bakeout lamps on. The sources are then heated up for about 2 to 4 hours to outgas. Residual gas analyzer scans are taken of the system to ensure that the water vapour pressure is too low to effect the film properties (Audas and Brodie, 1987). The substrate is adjusted to the temperature required for the deposition. The sources

are brought up to evaporation temperature and allowed to stabilize for 10 to 20 minutes. This also tends to getter the system, since the silicon reacts with excess water vapour. When the sources are stabilized, the silane gas is bled in and the pressure held constant for another 3 to 5 minutes after which the shutter is opened.

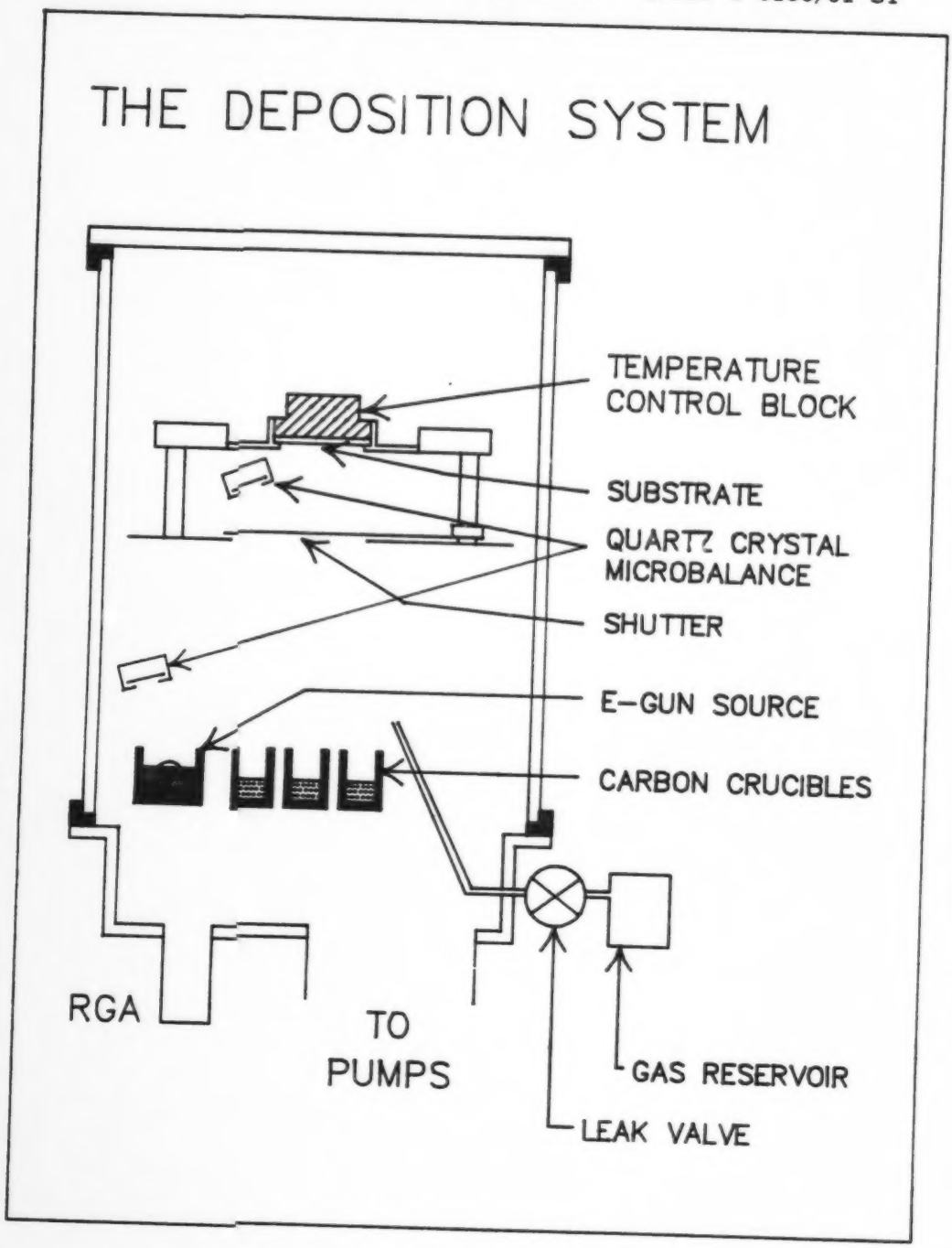

Figure 1. A schematic representation of the vacuum chamber.

3.2 Deposition Sources

3.2.1 Silicon

Silicon was deposited from a vitreous carbon crucible using a resistively heated tantalum source. Silicon was also deposited using an electron beam gun. The use of the vitreous carbon crucible introduces about 4 to 6 at% carbon. The e-beam deposition results in virtually clean Si within the experimental error of the Auger analysis. Although the carbon may be desirable (Carlson et al, 1987), it is useful to be able to control the carbon content. The e-beam source is required to evaporate the boron. The deposition rate was monitored with a quartz microbalance which was placed near the substrate. Si was deposited at a rate of about 0.5 nm/s.

3.2.2 Antimony

Antimony was deposited from an alumina crucible using a resistively heated Ta source. Antimony sublimates at a low temperature (T=700 K) and is easy to control. The deposition rate was controlled using a quartz microbalance placed about 10 cm above the source.

3.2.3 Indium

Indium was deposited from an alumina crucible using a resistively heated Ta source. Indium is clean, easy to handle and evaporates at a relatively low temperature (T=1010 K). The rate of deposition is controlled in the same fashion as the antimony.

3.2.4 Boron

Boron was initially deposited from a vitreous carbon crucible using a resistively heated Ta source. The temperature of sublimation for boron is high (T= 2070 K). This resulted in a very short lifetime for the sources and crucibles. To eliminate this problem, the boron was sublimated from the e-beam source. The rate of deposition was monitored by a quartz microbalance.

3.2.5 Phosphorus

Phosphorus was deposited from a vitreous carbon crucible using a resistively heated Ta source. The sublimation temperature for phosphorus is relatively low (T=870 K). This material is more difficult to handle, since it can react with water vapour to produce hazardous vapours. Red phosphorus was used because it is relatively stable and can be exposed to air for short periods of time. The main technical problem with phosphorus is its very low sticking coefficient.

Phosphorus "wanders" through the deposition system reducing the effectiveness of chimneys to keep the deposition chamber clean. The low sticking coefficient also means that the deposition rate can not be monitored using a quartz microbalance. It was necessary to "reactively" evaporate the silicon in a phosphorus ambient. This was achieved by first setting the phosphorus partial pressure using the phosphorus source temperature. When this was stable, the silane was introduced at much larger pressures than the phosphorus partial pressure.

3.3 Substrate and Heater

The a-Si films were deposited on Corning 7059 glass. The substrates are prepared by attaching thin teflon coated wires using a vacuum epoxy (Torr Seal) to physically hold them in place and silver paint for the electrical contact. This is achieved by vacuum depositing metal contacts over the silver paint and the Si film. A layer of silicon vacuum grease or fine graphite powder is placed between the substrate and the heater to provide good thermal contact. The grease is used for temperatures below 470 K and the graphite is used for higher temperatures. The heater also contains a liquid nitrogen chamber which allows it to be used to cool the substrate.

The thin film samples are deposited on the substrate in four parts at the same time. Masks are used during the deposition of the contacts and the Si to provide planar and sandwich conductivity samples.

Hall effect and Seebeck samples as well as a patch for optical bandgap measurements. are all deposited at the same time.

The devices were deposited on crystalline Si wafers and Corning 7059 glass. Contacts were made to the bottom of the crystalline wafers by indium solder. A thin film of molybdenum was used as the bottom contact for the samples deposited onto the 7059 glass. An 11x11 array of circular dots was used to make electrical contact to the top of the devices.

3.4 Gas Control

The NH_3 and SiH_4 were bled into the vacuum chamber via a precision sapphire on stainless steel leak valve. This valve, when employed with a gas reservoir, provides a very constant partial pressure. The NH_3 required pressures of $1x10^{-6}$ torr. This pressure was monitored during deposition with a residual gas analyzer (RGA) and fluctuations in the pressure were used to detect small changes in the evaporation rate. This allowed a very precise control of the deposition rate. The SiH_4 requires much higher pressures, sufficiently high to saturate the RGA. The ionization gauge was calibrated with the RGA at low pressures and used to monitor the silane at the higher pressures required for the production of "intrinsic" a-Si.

3.5 Anneal

The first anneal for the devices was carried out in situ at a $5x10^{-8}$ torr ambient pressure. Subsequent anneals were done in another vacuum chamber at about $5x10^{-6}$ torr. At the beginning of the contract period, the standard anneal was for about 30 min at 470 to 480 K. Yang and Lee (1986) suggested that the di-hydride phase could be removed by annealing to 520 K. Consequently all succeeding anneals were done at 500 K and above.

3.6 Hydrogen Evolution

The importance of removing the di-hydride phase, which is detrimental to the electrical properties, has led to the development of a hydrogen evolution apparatus. This consists of a 100 liter vacuum chamber which is pumped to 10^{-8} torr. A tantalum furnace was installed and it is supplied by a computer controlled variac power source. The computer is necessary to control the heating rate to a constant 11 K per minute. When the furnace, which is monitored by a type R thermocouple, reaches 370 K, the gate valve to the chamber is closed and the system pressure is measured at set intervals along with the sample temperature. The rate of hydrogen evolution at various temperatures shows the amount of each phase of hydrogen bonding (poly-hydride, di-hydride and mono-hydride) that was present in the sample. The outgassing rate of the

vacuum chamber is relatively constant and is subtracted out.

3.7 Seebeck Measurements

The Seebeck measurements are a reliable way to measure the carrier type. Due to multiple student users over a period of time, the Seebeck apparatus was not functioning optimally at the beginning of this work. Seebeck measurements for the very high resistance a-Si samples are more difficult to obtain than for some other samples. A special high input impedance and a low input offset current (10 fA) amplifier must be used. This means that all vacuum feedthroughs and wires must be cleaned properly to prevent leakage. A complete refit of this apparatus was necessary before these samples could be studied, and the carrier types identified.

3.8 Conductivity

The conductivity of the samples was measured in situ at pressures below 5×10^{-8}. The measurements were performed by applying 30 V across the two planar contacts on the sample and measuring the current using a 10^{-14} A resolution electrometer. The sample is cooled to 100 K and allowed to warm up under computer control at a slow rate. The conductivity is measured at precise intervals to a temperature of about 460 K. The high temperature activation energy is then obtained using an

Arrhenius plot. Many of the samples produce a straight line plot which indicates a well defined activation energy level for the sample.

3.9 I-V and C-V Characterization

The I-V characterization is used to test samples to see if a rectifying junction has been formed. The curves can also be analyzed to provide information on the series resistance, the shunt resistance and the quality factor of the device. When the solar cells are tested, the I-V characteristics will also provide a way to measure the short circuit current, the open circuit voltage, the maximum power, the fill factor and the cell efficiency. The C-V characterization provides information on the doping density in the depletion region.

4. Results and Discussion

4.1 NH_3 Compensation

4.1.1 Intrinsic

The a-Si thin films that are deposited in a vacuum of $6x10^{-8}$ torr have a high room temperature conductivity (10^{-3} S/cm), an activation energy of 0.15 ev and an optical bandgap of 1.4 eV. To reduce the number of gap states, hydrogen is added to the films. This hydrogen can be obtained from reactive evaporation in water vapour, ammonia, silane, etc. Samples of a-Si were prepared under various partial pressures of ammonia (NH_3) gas and several substrate temperatures. Figure 2 shows the effect of increasing the NH_3 content on the electrical conductivity. The three curves show that as the NH_3 content is increased, the Arrhenius plot of the sample conductivity more closely approaches "intrinsic" behavior. The "intrinsic" material has a well defined activation energy as seen by the straight Arrhenius plot and the activation energy (E_A= 0.9 eV) is about one half of the optical bandgap (E_0= 1.9 eV).

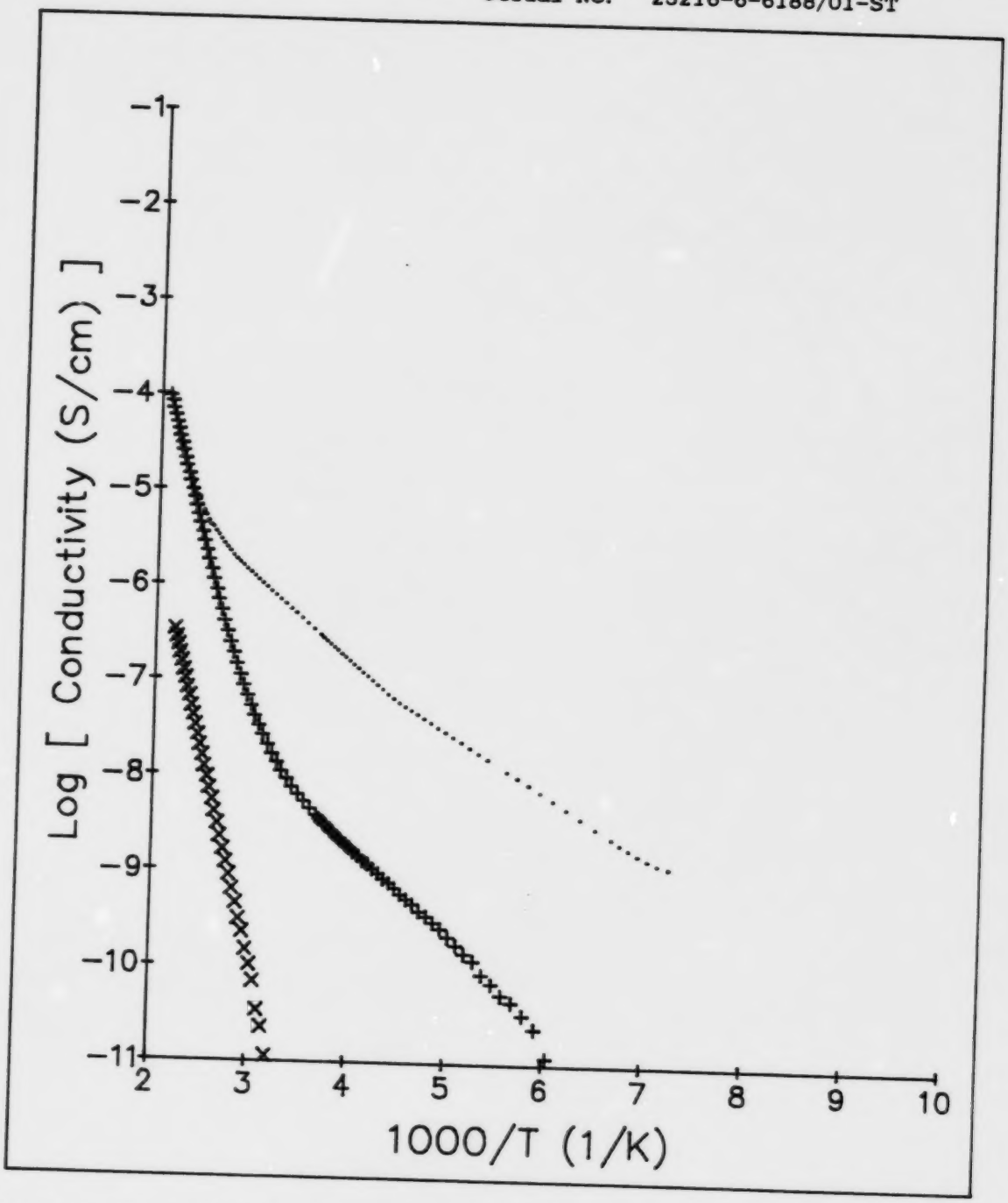

Figure 2. The effect of increasing NH_3 pressure present in the system during deposition. The curves represent samples deposited with no ammonia present (. 850807), $4x10^{-6}$ torr (+ 860402) and $2x10^{-5}$ torr (x 860410) ammonia.

4.1.2 N-type Doping

Co-evaporation with antimony was used to produce n-type a-Si. This produced samples with a room temperature conductivity which was dependant on the level of doping, with an n-type Seebeck coefficient. The material appeared to be "good" doped a-Si but all attempts to produce Schottky barriers failed. The use of high temperature substrates (600 K) did introduce a problem in that the antimony re-evaporated from the substrate, and reduced antimony concentrations were actually incorporated into the films.

4.1.3 P-Type Doping

Co-evaporation with indium was used to try to produce p-type a-Si films. The room temperature conductivity of the films graded with the doping level as expected but the Seebeck coefficient proved the films to be n-type. After many attempts using different values of T_s and anneal procedures, it was found that the indium would not produce a p-type material under these conditions.

4.1.4 Devices

The first all amorphous devices were attempted with no

success. a-Si on c-Si devices were produced but the assessment of the resulting data was ambiguous. It was not possible to determine definitively, whether the depletion region occurred in the amorphous silicon. Calculations of a depletion layer width using the doping densities in the two materials, amorphous and crystalline Si, suggested that it could be in the crystalline material. Another serious problem which curtailed this investigation was the unavailability of crystalline Si wafers with the necessary range of doping densities.

After much work and discussion, it was decided to try silane (SiH_4) as the reactive gas to provide the compensation.

4.2 SiH_4 Compensation

4.2.1 Intrinsic

To eliminate the nitrogen impurity which is inherent in the use of ammonia gas, samples were deposited in a silane (SiH_4) ambient. The sticking coefficient for silane is smaller than that of NH_3 hence the partial pressure of SiH_4 was set higher at $6x10^{-5}$ torr. This was measured using a calibrated ionization gauge since the RGA saturates at pressures lower than the pressures to be measured. These films were annealed at 500 K for about 2 hr and the resulting samples had room temperature conductivities of about 10^{-10} Scm^{-1}, high temperature

activation energies of 0.8 eV and optical bandgaps of 1.6 eV.

Figure 3 shows the effect of increasing the silane content on the conductivity of the vacuum deposited films. The samples were deposited in silane ambients of $3x10^{-6}$ torr (870202 x), $2x10^{-5}$ torr (870211 +) and $6x10^{-5}$ torr (870409 .). The Arrhenius plots are linear for the sample 870409 which suggests a well defined activation energy.

Further investigation, performed at the end of the contract period, showed that the hydrogen compensation of the a-Si:H:C films was not complete for samples used to fabricate devices. A further increase of the silane gas pressure coupled with a decrease in the substrate temperature during deposition, resulted in the reduction of the room temperature conductivity to about 10^{-12} S cm^{-1}. The high temperature activation energy also increased to 0.89 eV. This would explain much of the trouble initially encountered in reproducing working devices. If the compensation is not complete, then small variations in the deposition conditions would cause large changes in the film properties. It is necessary to saturate the film with hydrogen so that the doping efficiency is maximized and small changes in the deposition conditions do not change the film properties significantly.

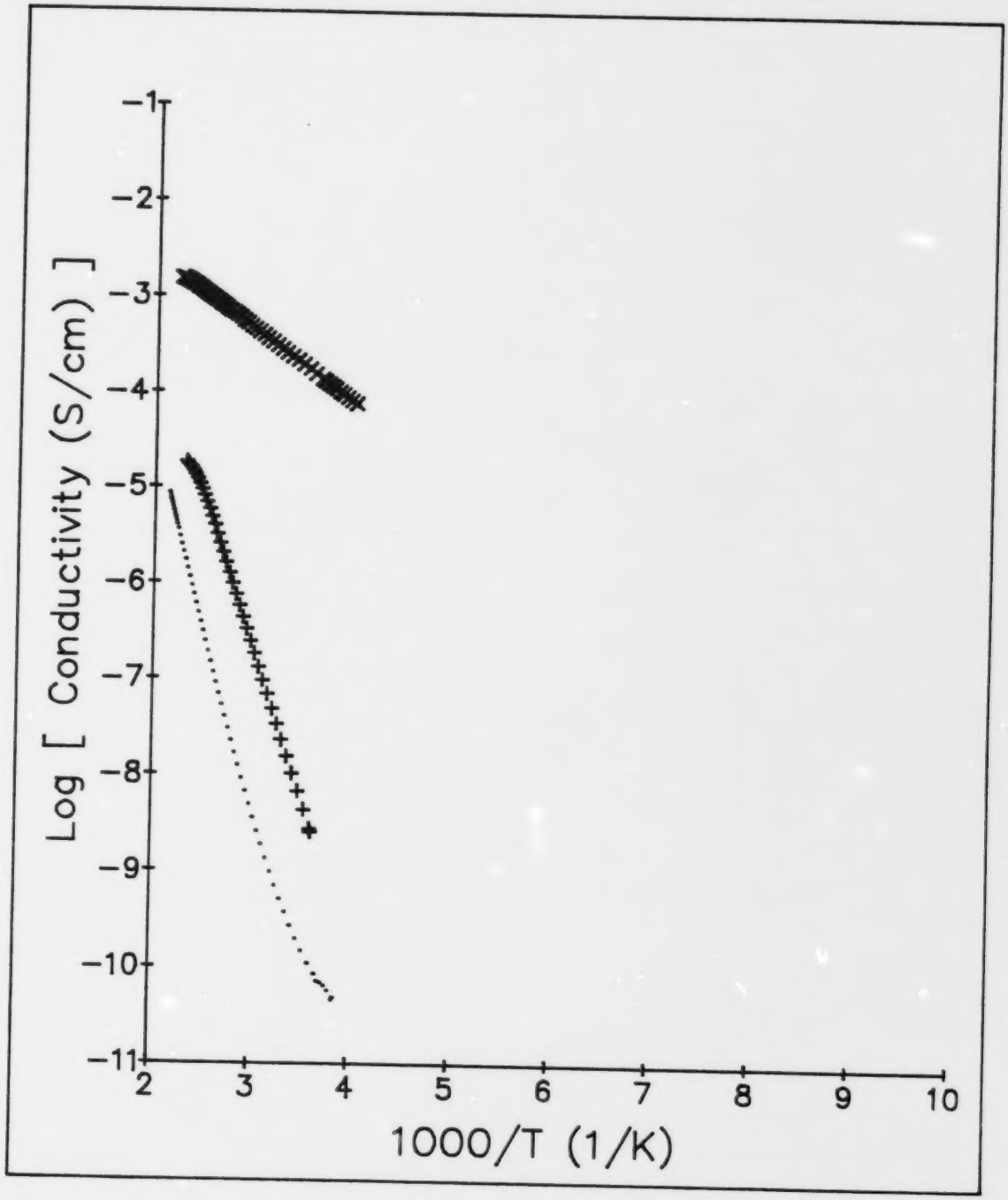

Figure 3. The effect of increasing the silane pressure on the conductivity of a-Si:H thin films. The samples were prepared with $3x10^{-6}$ torr (x 870202), $2x10^{-5}$ torr (+ 870211) and $6x10^{-5}$ torr (870409) silane partial pressure during deposition.

The analysis of the amount of silane which is captured in the growing film is similar to that derived for water vapour by Audas and Brodie (1987). The amount of silane present on the surface of the film will be related to the rate of arrival of silane molecules (partial pressure of silane) and the rate of re-evaporation of these molecules from the surface (substrate temperature) by an equation of the form (i.e. the number of molecules on the surface is just the arrival rate times the lifetime on the surface):

$$N_{SiH4} = C1 \times P_M(SiH_4) \times \exp(E_{AE} / kT_S)$$

Where N_{SiH4} is used to represent the number of "silane" molecules per unit area on the surface of the growing film at any instant in time, C1 is a function of the molecular mass and temperature of the silane gas, $P_M(SiH_4)$ is the partial pressure of silane (in torr) measured at the residual gas analyzer, k is the Boltzmann constant and T_S is the temperature of the substrate (in K) during deposition. The activation energy necessary to remove a silane molecule from the surface of the film (E_{AE}) is about 0.05 eV. This is very low compared to the value (water vapour E_{AE}=0.35 eV) which was found for water vapour. This means that to incorporate a set amount of hydrogen, the silane pressure must be much higher than that required to incorporate the hydrogen using water vapour. The above equation is used to describe the film contamination by the ambient gas since the Si condenses on the surface and each

monolayer of film should contain N_{SiH4} molecules of silane per square centimeter. The calculated value of the average lifetime of a silane molecule on the surface of the film is many orders of magnitude less than the time required to deposit a monolayer of Si for the smallest T_S used in these experiments. This would suggest that the rate of deposition of the Si is not important in the calculation of the amount of silane gas incorporated into the film. However, if the average lifetime for a silane molecule on the surface is long with respect to the time required to deposit a monolayer of Si, the value of N_{SiH4} would be inversely proportional to the deposition rate.

The value of C1 is calculated from the equation:

$$C1 = t_0 \times (6.28 \times M \times k \times T_G)^{-0.5}$$

Where M is the molecular weight of a silane molecule (32), T_G is the gas temperature (300 K) and t_0 is of the order of 10^{-13} s [7]. This yields a value of C1 equal to 3×10^{-11}. The value of N_{SiH4} is in molecules per square centimeter when the pressure is measured in torr.

Figure 4 shows the linear relationship between the activation energy and the preparation parameter $\log(N_{SiH4})$. The last sample prepared in September ($\log(N_{SiH4}) = -3.5$) shows that even these preparation conditions may not be sufficient to fully saturate the film with hydrogen, since even this point lies on the straight line. However, the film properties (activation energy and room temperature conductivity)

are similar to those of high quality films prepared by glow discharge techniques.

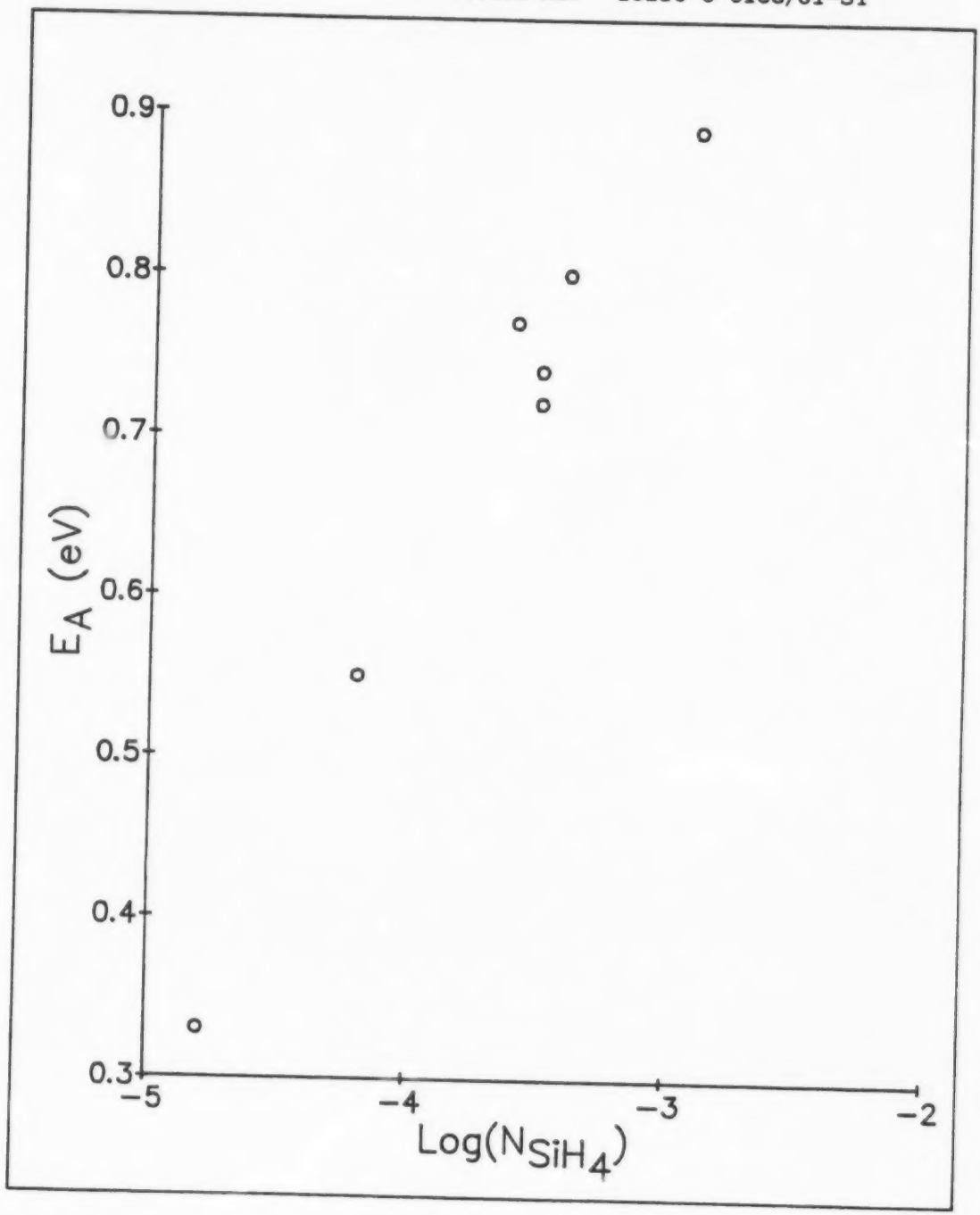

Figure 4. The effect of increasing the silane content on the activation energy of a-Si:H thin films. N_{SiH4} is a function of the partial pressure of silane and the substrate temperature.

4.2.2 N-Type

The use of antimony to dope the a-Si n-type yields similar results to that obtained for NH_3 compensated films. However, it was still not possible to make Schottky devices with this material. The Arrhenius plots of the conductivity data for these samples were not linear which suggests that there was not a well defined energy level. It has also been noted that antimony re-evaporates when deposited onto high temperature substrates making it difficult to introduce large concentrations of this dopant. A new dopant, phosphorus, was introduced.

Phosphorus is more difficult to co-evaporate and it was found that because of the low sticking co-efficient, the quartz microbalance could not be used to monitor the rate of deposition. After a number of test experiments, it was found that silicon has to be reactively evaporated in a phosphorus ambient, and the phosphorus content could be controlled by adjusting the phosphorus partial pressure. The room temperature conductivity of the phosphorus doped samples is about $4x10^{-6}$ S/cm while the activation energy is 0.48 eV. Seebeck experiments confirmed that the samples are n-type.

Figure 5 shows the effect of phosphorus doping on the conductivity of the film. Sample 870409 (.) is undoped, 870508 (+) lightly doped (0.2 at%) and 870520 (x) is more heavily doped (1.0 at%). These

values have been estimated from the deposition conditions and the doping will be known more accurately when the Auger data is available. This will also allow a calibration of phosphorus pressure versus the resultant doping concentration.

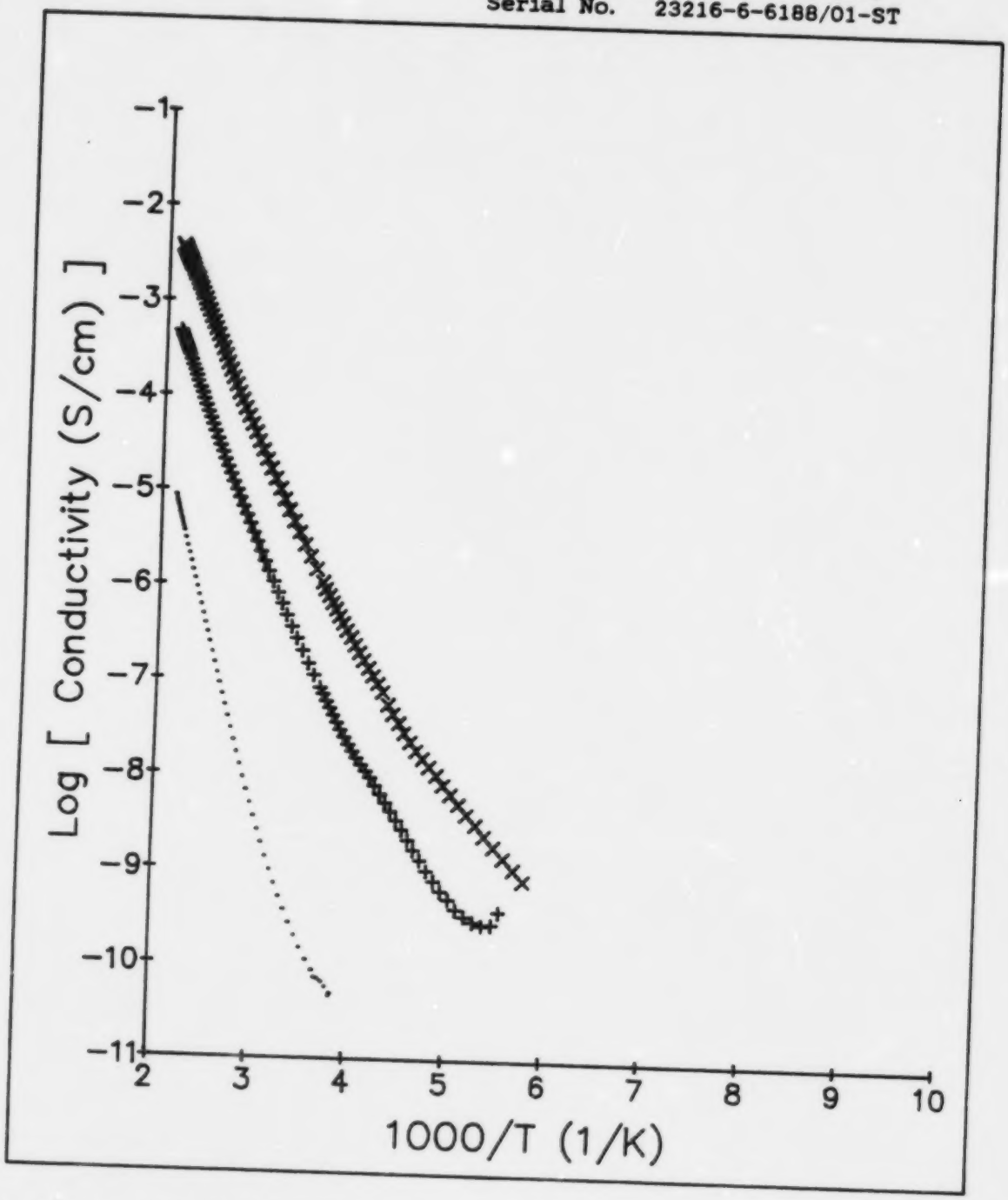

Figure 5. The effect of various levels of phosphorus doping on the conductivity of silane compensated films. Sample 870409 (.) is undoped. 870508 (+) the conductivity of the film. lightly doped (0.2 at%) and 870520 (x) is more heavily doped (1.0 at%).

4.2.4 P-Type

Attempts to fabricate p-type samples by co-evaporation with indium were not successful and the dopant was changed to boron.

Boron can be co-evaporated with Si to produce p-type films. The carrier sign was confirmed by Seebeck measurements. The high evaporation temperature required for boron makes it difficult to deposit pure material from a resistively heated crucible and an e-beam evaporation source was used. Typical values obtained for boron doped samples give a room temperature conductivity of $4x10^{-4}$ S/cm and an activation energy of 0.37 eV.

Figure 6 shows the effect of boron doping on the conductivity of the samples. The boron doped samples shown contain about 0 at% (. 870409), 1.5 at% (+ 870324) and 4.0 at% (x 870421).

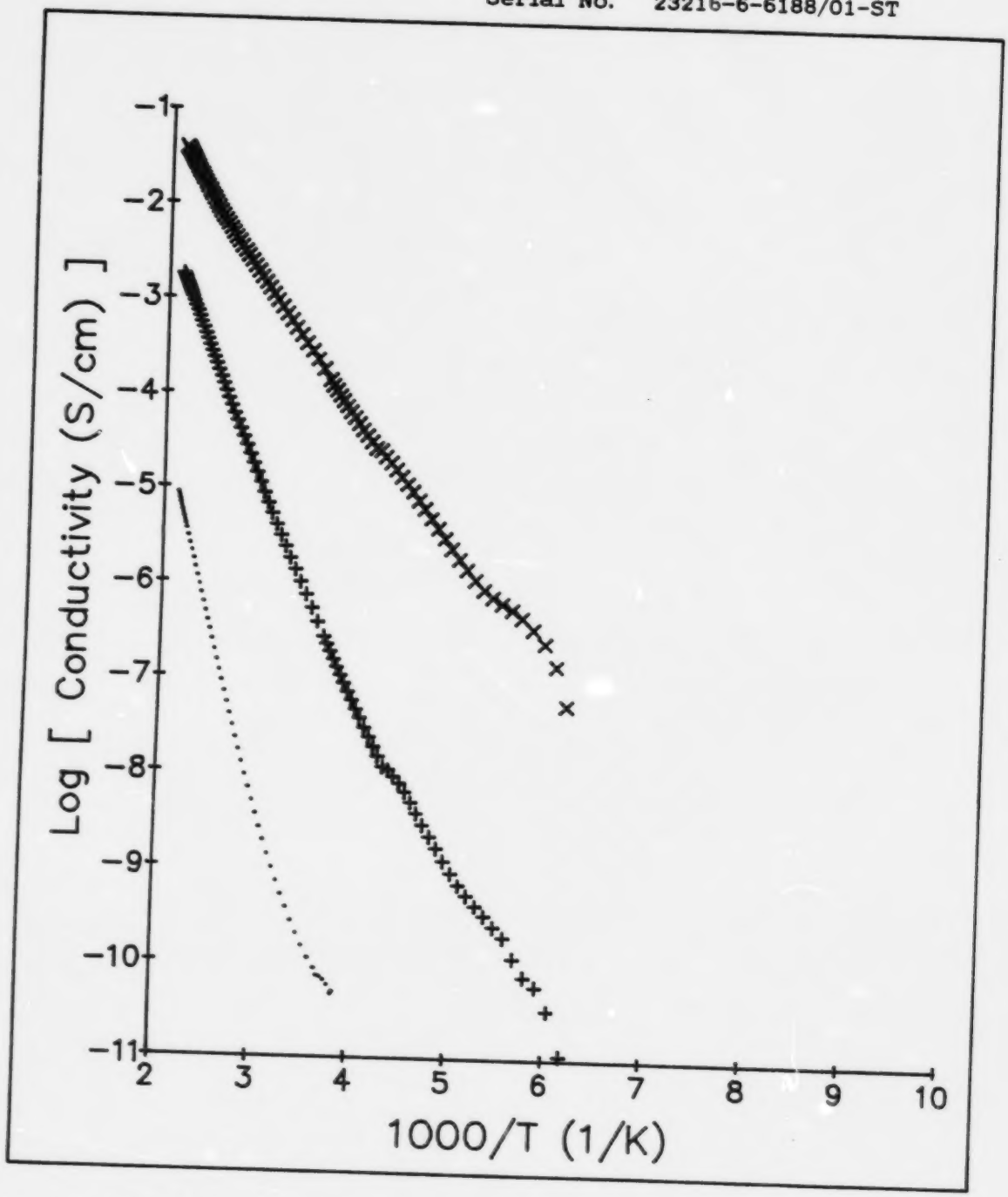

Figure 6. The effect of boron doping on the conductivity of silane compensated films. The boron doped samples shown contain about 0 at% (. 870409), 1.5 at% (+ 870324) and 4.0 at% (x 870421).

4.2.6 Devices

In the past six weeks this work has enabled the fabrication (to our knowledge for the first time) of all-amorphous a-Si:H diodes by a reactive evaporation process. Devices made to date have the p-i-n structure. They consist of a 30 nm p-type layer, 300 nm intrinsic layer and a 30 nm n-type layer. The top and bottom contacts are molybdenum. The substrate is held at 420 K during the deposition and the shutter is closed between layers while the sources are stabilized. The phosphorus doped layer is deposited first because of the difficulty of adjusting the doping rate conditions.

The anneal procedure is very important in the fabrication of these devices. The standard 2 hr anneal at 480 K produces I-V characteristics which are ohmic. A further 2 hr anneal at 500 K results in the I-V characteristics being non-ohmic but the curve is essentially symmetric about the origin, and showed no distinct forward or reverse bias. However an anneal over night (19 hr) at 500 K produced rather good I-V characteristics. In Figure 7, we see the I-V characteristics of a p-i-n device. The series resistance (R_S) of this sample is 2.4 kohms and the shunt resistance (R_{Sh}) is 680 kohms. The high R_S makes it difficult to determine the correct quality factor (n).

4.3 Solar Cells

The diodes fabricated to date use 3 mm diameter metal dots of opaque metal as the top contact. A weak sensitivity to high intensity light (about AM1, 100 mW/cm^2) can be seen by illuminating the edge of the contact.

There was some difficulty in reproducing the devices which were fabricated early in the summer. This was believed to be caused by incomplete compensation of the a-Si. For films that are not completely compensated, (i.e. do not contain sufficient hydrogen) it is expected that the anneal procedure will be very important. Some of the di-hydride phase is converted to the compensating mono-hydride phase if the anneal is performed at a low (500 K) temperature over an extended period of time. See section 4.2.1. The latter work on this contract was directed toward the necessary task of verifying this hypothesis and there was no time left to fabricate test solar cells. However, it is believed that solar cells can be fabricated by this process.

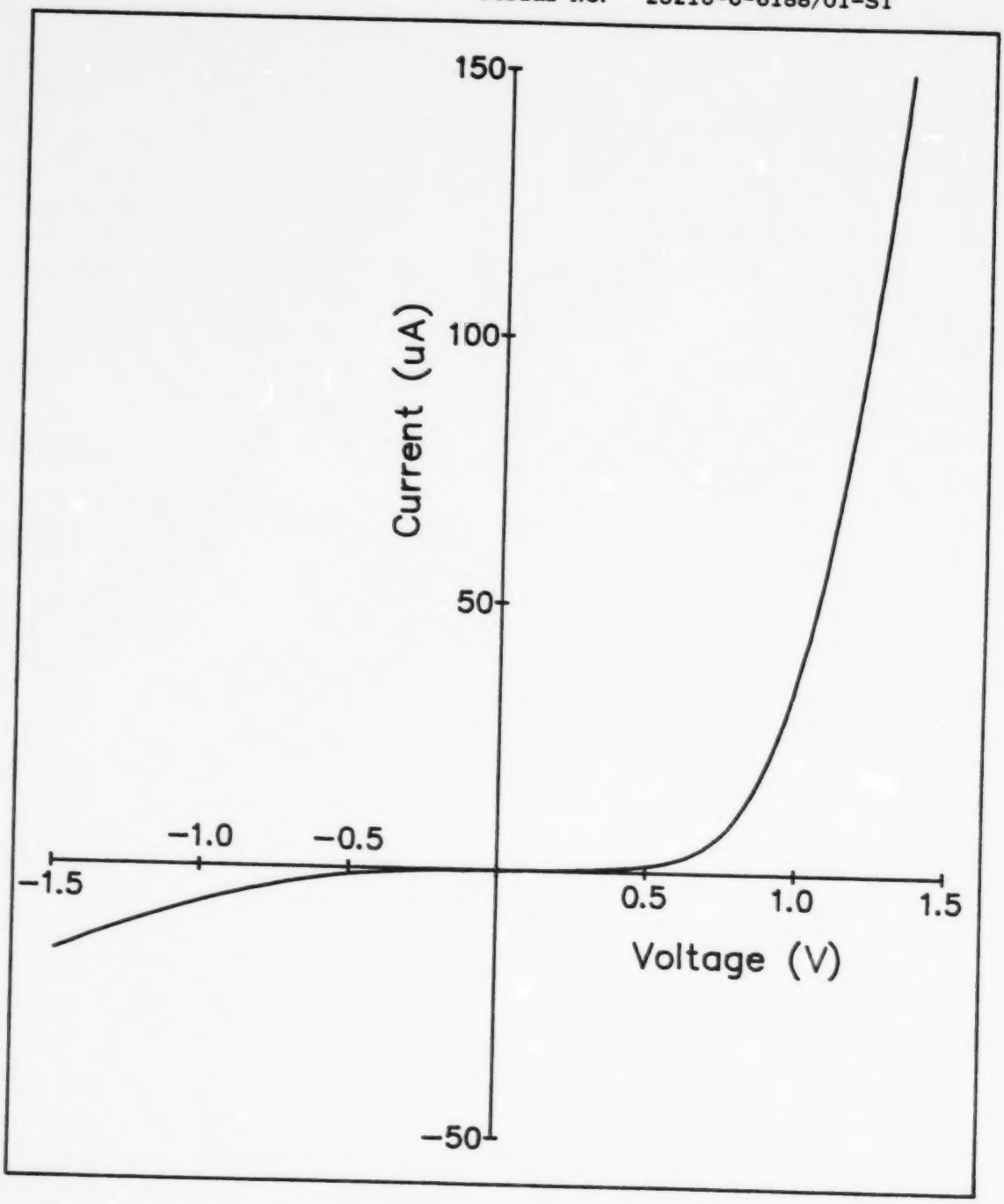

Figure 7. The I-V characteristics of a p-i-n device which was annealed for 19 hr at 500 K.

4.4 Hydrogen Evolution

It is necessary to know the hydrogen content of the samples and the form of the hydrogen bonds to better understand the effects of the many deposition parameters on the film properties. To obtain this information, a hydrogen evolution experiment was developed. The sample is heated at about 10 K/min from room temperature to 1100 K. The hydrogen is driven off at certain temperatures which depend on the bond type. Generally it is known that a plot of the rate of hydrogen evolution vs. temperature shows up to 4 peaks. These consist of a peak at low temperatures for the poly-hydride, a peak at about 660 K resulting from the di-hydrides, a peak at about 900 K for the mono-hydride phase and finally a sharp peak at about 1000 K for the last hydrogen driven out by the crystallization of the sample.

This technique allows us to investigate the amount of hydrogen which is incorporated into a sample, for a given set of preparation conditions, and the type of bonds that it forms. It is important to have most of the hydrogen incorporated in the mono-hydride phase since this is the "active" form which removes gap states, and at the same time yields the best electronic properties for photovoltaic devices. The effects of the anneal procedure on the proportion of hydrogen in each of the three phases can be investigated by this

technique.

Figure 8 shows a plot of the hydrogen evolution rate vs temperature for a sample (870319) which has undergone a 2 hr anneal at about 500 K. A two hour anneal at 500 K appears to be equivalent to a 1 min anneal at 660 K for the removal of the di-hydride bonded hydrogen. The absence of poly- and di-hydride peaks suggests that this anneal process should be sufficient if there is enough mono-hydride present in the film.

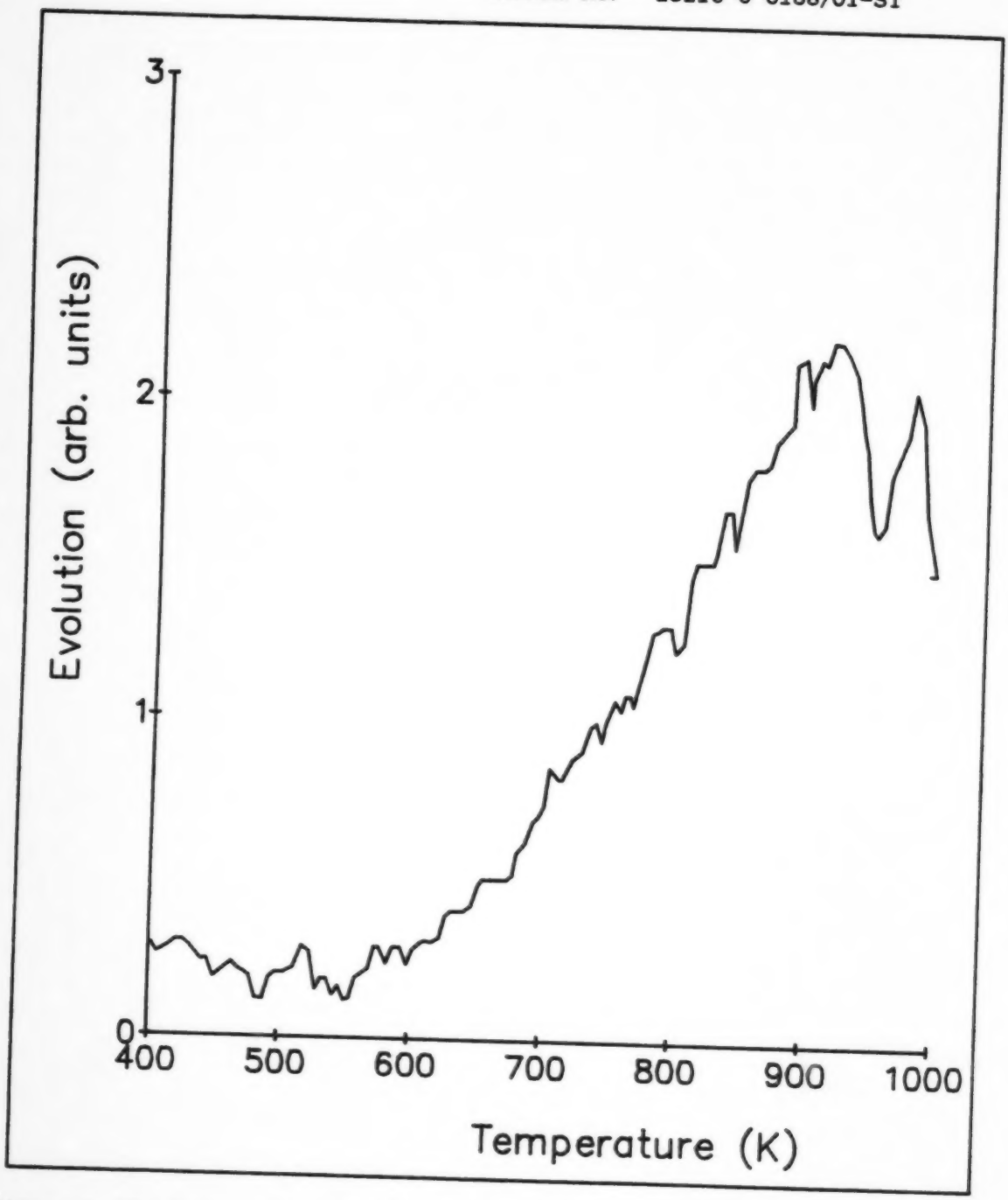

Figure 8. The hydrogen evolution rate vs temperature for sample 870319 which has undergone a 2 hr anneal at 500 K. Note the presence of a broad monohydride peak and a sharp recrystallization peak.

5. Conclusions

5.1 NH_3

The ammonia compensated films did not produce devices. However, the ammonia compensated films were not doped with boron or phosphorus. It is not known if these dopants would produce working devices with ammonia compensation. Some nitrogen in the samples stabilizes the material and reduces or eliminates the Staebler-Wronski (S-W) instability (Thomas, 1985). It would be of interest to prepare samples with ammonia and silane gases present in various proportions to see if this is possible. If a relatively small amount of nitrogen can accomplish this, the electronic properties of the resulting films may still be acceptable for solar cell applications.

5.2 SiH_4

Samples prepared with silane present in the system during deposition showed "intrinsic" electrical properties. The SiH_4 gas pressure was typically $3x10^{-5}$ torr with a deposition rate of 0.5 nm/s. For these films the high temperature activation energy was (E_A=0.8 eV),

about half of the optical bandgap (E_0=1.6 eV). The samples co-evaporated with antimony had low activation energies (E_A=0.2 eV), high room temperature conductivities (10^{-4} S/cm) and n-type Seebeck coefficients. The indium doping resulted in a similar change in properties. However, the fact that the indium "doping" produced n-type samples, led to the use of boron as a p-type dopant. Schottky barriers could not be formed using the antimony doped samples. Antimony re-evaporates from high temperature substrates and the Arrhenius plots of the conductivity do not produce a straight line as expected for a well defined activation energy. The low sublimation temperature of antimony creates a problem because high temperature anneals are required in the sample production. Phosphorus was introduced as the n-type dopant.

It was found that a substrate temperature of 420 K during the deposition and an anneal at 500 K for 2 hr was sufficient to produce "intrinsic-like" a-Si. It may be that the addition of small amounts of NH_3 during deposition can reduce the S-W effect. Work performed in the last month of the contract period showed that pressures of $2x10^{-4}$ torr and substrate temperatures of 320 K with the above anneal produces samples with better activation energies and lower room temperature conductivities.

5.3 Devices

The a-Si on c-Si devices which were produced at the

beginning of the contract were of limited use because the results were not conclusive. It was not possible to determine whether the depletion region occurred in the crystalline or the amorphous Si.

It was possible to produce all amorphous Si devices with the use of silane compensation and boron and phosphorus doping. The production of devices required an anneal procedure. It was found that an anneal at 500 K for 17 hr will produce working p-i-n diodes. Initially the devices prepared were marginally compensated by silane and working devices were difficult to reproduce. Much of the work has been done to optimize the silane compensation needed to fabricated devices reproducibly.

5.4 Summary

The possibility of fabricating all amorphous diodes by a reactive evaporation process has been demonstrated for the first time. This method uses only relatively safe materials employed in a normal laboratory environment with no special safety facilities beyond those required for normal good laboratory practices.

The photoelectronic stability of these materials has not yet been investigated. However, the method is such that a variety of possible stabilizing elements can be introduced, simply and in a controlled way, if that should prove to be necessary.

6. Recommendations

The possibility of device fabrication has been demonstrated but there has been very little time to improve or optimize the materials properties. This may be accomplished in several ways. A number of studies remain to be done before several essential questions can be answered. It is recommended that this work be continued in order to provide answers to the questions posed here, and hence build on the breakthrough identified in this report.

The effects of the anneal procedure on sample and device properties is not yet well understood, although it is likely related to the way that the hydrogen is bonded. The work with the hydrogen evolution experiments will help clarify the effects of the anneal procedure on the hydrogen content and bonding configuration. This work should require a few months to complete.

Carbon contamination of the a-Si films is present due to the use of a vitreous carbon crucible. The use of another e-beam evaporation source in the vacuum chamber would allow us to deposit both Si and boron simultaneously and control the carbon content in the devices.

The doping of the silicon has not been optimized for the use

of boron and phosphorus. A series of samples should be prepared to obtain a quantitative measure of the doping efficiencies. This would require the fabrication of a series of samples with different doping levels followed by a complete characterization of their properties. This would allow us to optimize the doping level required for each dopant

The addition of small amounts of NH_3 could be added to test the stabilizing effects of nitrogen on the S-W effect. This would require that a series of samples be made with various proportions of silane and ammonia gas present during deposition. The effects of the nitrogen on the doped material properties and on the devices should be investigated.

The physical structure of the p-i-n device has not been optimized. Varying the layer thickness and measuring its effects on the device characteristics is necessary to maximize the solar cell output.

The fabrication of Schottky barriers and p-n devices will increase our understanding of the materials and the processes.

The amount of silane in the samples must be adequate to provide complete compensation. Large partial pressures of silane are therefore necessary during deposition. The use of a high temperature substrate during deposition may produce better samples although it will make it more difficult to increase the silane content. The high substrate temperature should allow only the mono-hydride phase of the hydrogen to be incorporated during the deposition process. This would eliminate the

anneal process that has been required to complete the devices. However, more work is required to solve the technical difficulties created by the higher substrate temperatures (T_S= 520 K) related to the incorporation of enough dopants and the reactive gas into the various layers. It is believed that these problems can be solved.

There is obviously much work to be done in this field now that the initial breakthrough has been made by producing all amorphous Si devices by a reactive evaporation process.

7. References

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8. Appendix I - Sample List

Sample	Note	%Dop	Dop	Rate (A/sec)	Contacts Top	Contacts Bot	Substrate Source	Substrate	Ea (eV)	Eo (eV)	Cond.rt	Ts (C)	P_M (torr)	Gas	Pb (torr)
860714	n-Si		Sb	0.0	AuCr	c-Si	eb	p-type				290	8E-08	NH3	1E-05
860827	i-Si			0.0		Mo	eb	7059				530			4E-07
860903	i-Si			0.0		Mo	eb	7059				530			8E-07
860910	i-Si			0.0		Mo	eb	7059				285			3E-07
860923	i-Si			0.0		AuCr	vc	7059				115			3E-07
861029	p-Si		In	5.2	AuCr	AuCr	vc	7059				380	4E-06	NH3	5E-06
861031	p-Si		In	5.2		Mo	vc	7059				420	4E-06	NH3	4E-06
861103	p-Si	2.3	In	0.0	In	Mo	vc	7059				390	4E-06	NH3	4E-06
861105	p-Si	1.5	In	4.2	In	Mo	vc	7059				400	4E-06	NH3	5E-06
861106	i-Si			4.2	In	Mo	vc	7059				400	4E-06	NH3	5E-06
861112	p-Si	5.8	In	0.0	In	Mo	vc	7059				400	4E-06	NH3	3E-06
861119	n-Si	1.9	Sb	0.0	Al		vc	7059				400	4E-06	NH3	4E-06
861125	p-Si		Sn	0.0	Al		vc	7059				400	4E-06	NH3	4E-06
861127	n-Si		Sb	0.0	Al		vc	7059				370	4E-06	NH3	4E-06
870202	i-Si			4.7	AuCr	AuCr	vc	7059	0.33		2.8E-04	110	1.5E-06	SiH4	3E-06
870211	i-Si			0.8	AuCr	AuCr	vc	7059	0.55	1.65	2.9E-07	275	1E-05	SiH4	2E-05
870216	i-Si			5.2	AuCr	AuCr	vc	7059	0.80	1.62	8.3E-10	210	5.5E-05	SiH4	1E-04
870219	i-Si			3.3	AuCr		vc	7059		1.64		295	5.5E-05	SiH4	1E-04
870221	p-Si		In	7.0	AuCr		vc	7059				300	2.6E-05	SiH4	5E-05
870225	i-Si	150V		6.4		AuCr	vc	7059	0.72	1.58	1.3E-09	305	5.5E-05	SiH4	1E-04
870227	i-Si	225V		6.2		AuCr	vc	7059	0.74	1.59	1.7E-09	295	5.5E-05	SiH4	1E-04
870305	p-Si	130V	In	7.5		AuCr	vc	7059	0.43		2.2E-04	305	5.5E-05	SiH4	1E-04
870310	i-Si	0.0	B	6.4		AuCr	vc	7059	0.70		2.7E-09	300	5.5E-05	SiH4	1E-04
870313	i-Si	0.0	B	5.5		AuCr	vc	7059	0.73		4.6E-09	300		SiH4	8E-05
870318	p-Si	0.2	B	8.3	AuCr		vc	7059				190		SiH4	8E-05
870319	p-Si	0.2	B	5.4		AuCr	vc	7059	0.10		4.3E-06	310		SiH4	2E-05
870324	p-Si	1.5	B	5.4		AuCr	vc	7059	0.51		1E-06	285		SiH4	1E-04
870331	p-Si	0.8	B	4.5	Ni		vc	7059	0.60		2.2E-08	285		SiH4	1E-04
870402	p-Si	0.3	B	0.0	Ni		vc	7059	0.71		4E-09	170		SiH4	1E-04
870407	i-Si peeled			0.0		Mo	vc	7059	0.89		2E-06	155	3E-05	SiH4	6E-05
870409	i-Si			5.4		Mo	vc	7059	0.77		2.7E-10	155	3E-05	SiH4	6E-05
870414	p-Si B+Si in crucible	0.0	B	5.0		Mo	vc	7059	0.90		1.1E-08	155	3E-05	SiH4	6E-05
870421	p-Si	4.0	B	5.7	AuCr	AuCr	vc	7059	0.37		3.5E-04	160	3E-05	SiH4	6E-05
870501	n-Si	3.5	Sb	3.8	AuCr	Mo	vc	7059	0.83		1.4E-07	145	3E-05	SiH4	6E-05
870508	n-Si	0.2	P	4.2	Mo		vc	7059	0.53		2.8E-07	150	3E-05	SiH4	6E-05
870514	n-Si	0.8	P	3.8	Mo		vc	7059	0.42		2.4E-06	155	3E-05	SiH4	6E-05
870520	n-Si	1.0	P	3.5	Mo		vc	7059	0.48		3.6E-06	155	3E-05	SiH4	6E-05
870525	n-Si		P	3.9	Mo		vc	7059	0.50		4.5E-06	155	3E-05	SiH4	6E-05
870529	n-Si		P	2.9	Mo		vc	7059	0.46		6.3E-06	150	4E-05	SiH4	9E-05
870603	n-Si		P	2.5	Mo		vc	7059	0.44		1.1E-05	150	3E-05	SiH4	6E-05
870605	n-Si		P	3.6	Mo		vc	7059				150	4E-05	SiH4	8E-05

870709	i-Si HE study		vc	7059				3E-05	SiH4	7E-05
870903	i-Si	Mo	vc	7059	0.89	5E-12	51		SiH4	2E-04

9. Appendix II - Device List

Sample	Note	Substrate Source		Ts (°C)	Rate (A/s)	p (torr)	Gas	p_b (torr)	Thic (A)	Dopants Top	Dopants Bot
860704	(c-Si/n-Si/AuCr)	eb	p-type			8E-06	NH3	1E-05			
860707	(c-Si/i-Si/AuCr)	eb	p-type	290		8E-06	NH3	2E-05			
860710	(c-Si/i-Si/AuCr)	eb	p-type	300		8E-08	NH3	1E-05			
860714	(c-Si/n-Si/AuCr)	eb	p-type	290		8E-08	NH3	1E-05			
860721	(c-Si/n-Si/i-Si/AuCr)	eb	p-type	260		8E-08	NH3	1E-05		Sb	
861016	(c-Si/n-Si/AuCr)	vc	p-type	380			none			Sb	
861022	(c-Si/n-Si/AuCr)	vc	p-type	400		4E-06	NH3	5E-06		Sb	
861024	(c-Si/i-Si/AuCr)	vc	p-type	400		4E-06	NH3	3E-06			
870107	(c-Si/Au)	vc	p-type	90			none	1E-07			
870108	(c-Si/Al/Al,Au,Sb)	vc	p-type	60			none	1E-07			
870114	(Mo/SiOx/i-Si/AuCr/SiOx)	vc	7059	110		4E-06	NH3	1E-05			
870123	(Mo/SiOx/n-Si/AuCr/SiOx)	vc	7059	310		4E-06	NH3	6E-06		Sb	
870424	(Mo/p-Si/i-Si/n-Si/AuCr)	vc	7059	155	4.0	3E-05	SiH4	6E-05	4800	B	Sb
870429	(Mo/n-Si/i-Si/p-Si/AuCr)	vc	7059	140	3.6	3E-05	SiH4	6E-05	4300	Sb	B
870510	(Mo/n-Si/i-Si/p-Si/Mo)	vc	7059	150	3.8	3.5E-05	SiH4	7E-05	4100	P	B
870519	(Mo/n-Si/i-Si/p-Si/AuCr)	vc	7059	150	3.5	3E-05	SiH4	6E-05	2800	P	B
870624	(Mo/n-Si/i-Si/p-Si/Mo)	vc	7059	150	3.6	3E-05	SiH4	6E-05	3900	P	B
870701	(Mo/n-Si/i-Si/p-Si/Mo)	vc	7059	150	3.9	3E-05	SiH4	6E-05	3700	P	B